CLAIMS

[Claim(s)]

[Claim 1]Usually, a stopping method of a phosphoric acid fuel cell lowering power generation temperature of a fuel cell body rather than usual, or having an adjustment power generation procedure of making a steam partial pressure increasing and generating rather than usual while shifting to a power generation stop state from a power generation state.

[Claim 2]A stopping method of the phosphoric acid fuel cell according to claim 1, wherein said adjustment power generation procedure is what is generated so that equilibrium concentration of phosphoric acid may turn into prescribed concentration.

[Claim 3]A stopping method of the phosphoric acid fuel cell according to claim 1 or 2, wherein said adjustment power generation procedure is what uses external energy.

[Claim 4]A stopping method of the phosphoric acid fuel cell according to any one of claims 1 to 3 which said phosphoric acid fuel cell is provided with a reformer made to generate hydrogen from hydrocarbon and water, and is characterized by said adjustment power generation procedure being a thing to which the steam/fuel ratio in refining original fuel gas to this reformer are made to increase from usual.

[Claim 5]A stopping method of the phosphoric acid fuel cell according to any one of claims 1 to 4, wherein said adjustment power generation procedure is a thing to which a ratio of oxygen utilization or hydrogen utilization is made to increase from usual.

[Claim 6]While said phosphoric acid fuel cell is provided with dummy load and further usually shifting to a power generation stop state from a power generation state, A stopping method of the phosphoric acid fuel cell according to any one of claims 1 to 5, wherein it connects generated output to this dummy load and electric power required for operation of said phosphoric acid fuel cell is provided with an electric power supply procedure supplied from the outside.

[Claim 7]A stopping method of the phosphoric acid fuel cell according to claim 6, wherein said electric power supply procedure is what controls resistance of said dummy load in a range in which power generation voltage of said phosphoric acid fuel cell does not rise rather than a specified value.

[Claim 8]A stopping method of a phosphoric acid fuel cell provided with a purge procedure which supplies a steam into inactive gas which purges a fuel cell body since it shifts to a power generation stop state.

[Claim 9]A stopping method of the phosphoric acid fuel cell according to claim 8, wherein said purge procedure is what supplies a steam at temperature after power generation stop completion so that equilibrium concentration of phosphoric acid may turn into prescribed concentration.

[Claim 10]A phosphoric acid fuel cell having a line which supplies a steam from this steam generator into an air pole supply air in a phosphoric acid fuel cell provided with a steam generator.

[Claim 11]A phosphoric acid fuel cell characterized by having a line which supplies this steam generator to a steam into reformed gas of a fuel electrode entrance from an exit of a reformer made to generate hydrogen from hydrocarbon and water in a phosphoric acid fuel cell provided with a steam generator.

[Claim 12]A phosphoric acid fuel cell having a line which supplies a steam from this steam generator into purge gas in a phosphoric acid fuel cell provided with a steam generator.
[Claim 13]A phosphoric acid fuel cell having a line which supplies at least a part of purge gas via inside of this steam generator in a phosphoric acid fuel cell provided with a steam generator.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the method of stopping power generation in the state where phosphoric acid is not frozen even if it does not keep it warm at the time of the stopping method of a phosphoric acid fuel cell, especially prolonged storage, and the phosphoric acid fuel cell for it.
[0002]
[Description of the Prior Art]Conventionally, the phosphoric acid fuel cell uses thick phosphoric acid as an electrolyte, and the usually employed density range is nearly 100%. The freezing temperature of phosphoric acid in the concentration of this neighborhood is near 40 ** (in 100%, it is 42.4 ** and referring to drawing 2). In the power generation state, since the temperature of a fuel cell body is as high as 150-200 ** (usually about 200 **), there is no possibility that phosphoric acid may freeze over, but if temperature falls even to a room temperature level when power generation is suspended, phosphoric acid is frozen and having serious influence on the characteristic of a fuel cell body is known.
[0003]When stopping a fuel cell temporarily, the measure of keeping a fuel cell body warm using a heater and other heating methods in order to prevent the characteristics degradation by this freezing is taken. When [required for incubation] energy source (power supply etc.) reservation cannot be carried out, or when a stop covers a long time, it is necessary to adjust phosphoric acid concentration to the low concentration which is a grade which phosphoric acid does not freeze from an economical viewpoint even if it does not carry out incubation. For example, if phosphoric acid concentration is reduced to about 78%, freezing temperature will fall to 0 ** (refer to drawing 2).
[0004]For this reason, phosphoric acid concentration is conventionally lowered after the power generation stop by holding a fuel cell body in a predetermined temperature and the atmosphere of a steam partial pressure. The conditions for making phosphoric acid into predetermined concentration can be searched for from the relation (refer to drawing 3) of the concentration of phosphoric acid, temperature, and the steam partial pressure on phosphoric acid. Setting out of a steam partial pressure is performed by circulating the gas which has a predetermined steam partial pressure to a fuel cell body.
[0005]For example, in JP,H7-169475,A, The method of carrying out humidification by the hygroscopic surface moisture in the air by introducing air into an air pole after a plant power generation stop is indicated, Hydrogen is introduced into a hydrogen pole after a plant power generation stop, a power generation reaction is caused in oxygen and the low temperature in the air of an air pole, and the method of diluting phosphoric acid concentration with the moisture generated as a result is indicated.
[0006]
[Problem to be solved by the invention]However, in the case of the air condition (a steam partial pressure is low) dramatically dried like winter, enforcement is difficult in order to use the gas which tends to be influenced by the open air conditions of the water vapor of the air in conventional technology. By the time the steam amount of supply to a fuel cell body decreases

and it reaches predetermined phosphoric acid concentration when a steam partial pressure is low even if it is a level of a feasible steam partial pressure, between a long time, for example, one to two days, may be needed dramatically, and there is a demerit in the field of personnel expenses and a power cost.

[0007]Also when introducing hydrogen after stopping a plant, there is a demerit that expense of hydrogen itself, expense of hydrogen supply equipment, etc. are needed. An object of this invention is to provide a stopping method of a phosphoric acid fuel cell and a phosphoric acid fuel cell which can perform phosphoric acid concentration adjustment before prolonged storage of a phosphoric acid fuel cell economically and simple.

[0008]

[Means for solving problem]While usually shifting to a power generation stop state from a power generation state, a stopping method of a phosphoric acid fuel cell of this invention lowers power generation temperature of a fuel cell body rather than usual, or is provided with an adjustment power generation procedure of making a steam partial pressure increasing and generating rather than usual. Since that it is what is generated so that equilibrium concentration of phosphoric acid may turn into prescribed concentration can make a predetermined thing phosphoric acid concentration after a power generation stop, said adjustment power generation procedure has it. [preferred]

[0009]Since that it is what uses external energy can compensate an insufficiency of a steam, said adjustment power generation procedure has it. [preferred] Said adjustment power generation procedure can increase a steam partial pressure because it is a thing to which that it is a thing to which the steam/fuel ratio in refining original fuel gas to this reformer are made to increase from usual, a ratio of oxygen utilization, or hydrogen utilization is made to increase from usual. Generated output can be connected to dummy load and the electric power required for operation of said phosphoric acid fuel cell can perform an adjustment power generation procedure in a low generation output by having an electric power supply procedure supplied from the outside.

[0010]Said electric power supply procedure can avoid that voltage of a fuel cell body rises too much, and a catalyst of a fuel cell body deteriorates because it is that by which power generation voltage of said phosphoric acid fuel cell controls resistance of said dummy load in a range which does not go up rather than a specified value. Since a stopping method of a phosphoric acid fuel cell of this invention shifts to a power generation stop state, it is provided with a purge procedure which supplies a steam into inactive gas which purges a fuel cell body.

[0011]At temperature after power generation stop completion, since that it is what supplies a steam so that equilibrium concentration of phosphoric acid may turn into prescribed concentration can make a predetermined thing phosphoric acid concentration after a power generation stop, said purge procedure has it. [preferred] A phosphoric acid fuel cell of this invention is a phosphoric acid fuel cell provided with a steam generator, and in an air pole supply air in reformed gas of a fuel electrode entrance from a reformer exit, Or a stopping method of the above-mentioned phosphoric acid fuel cell which is provided with a line which supplies a steam from said steam generator, and increases a steam partial pressure of a fuel cell body rather than usual by this into purge gas is realizable. In a phosphoric acid fuel cell provided with a steam generator, a phosphoric acid fuel cell of this invention is provided with a line which supplies at least a part of purge gas via inside of this steam generator.

[0012]

[Mode for carrying out the invention]The basic constitution of a phosphoric acid fuel cell is first explained using drawing 1. The fuel cell body 1 has structure which sandwiches the matrix 4 with the air pole 2 and the fuel electrode 3. The air which is the open air is supplied to the air pole 2, a part of oxygen is consumed by power generation, and the remaining air is exhausted. The gas which uses hydrogen as the main ingredients from CO transformer 5 is supplied to the fuel electrode 3, a part of hydrogen is consumed and the remainder is supplied to the burner 8 for reformers. The matrix 4 is a sheet in which the solution of phosphoric acid used as an electrolysis solution has sunk in. The fuel cell body 1 is cooled with the water from the steam separator 6. The water for this cooling will be heated conversely, will contain a steam, is

returned to the steam separator 6, and is separated from water. Therefore, this steam separator 6 is a steam generator. The raw materials and mineral fuel of gas which result in the fuel electrode 3 are hydrocarbon, such as town gas and LPG, and the reformer 7 is supplied with the steam supplied via the line L2 from the steam separator 6, become hot by the burner 8 for reformers, and the next chemical reaction is caused, CH_4+H_2O -> $CO+3H_2$ ... (1) $CO+H_2O$ -> CO_2+H_2 ... (2) hydrogen, CO, and CO_2 are generated. In this stage, the ratio of CO and CO_2 is about 10% respectively. And the reaction of (2) is further advanced by following CO transformer 5, and the ratio of CO is lowered even to about 1% by it. Since CO in fuel reduces the activity of the catalyst of the fuel cell body 1 (CO poisoning), making the ratio of CO small has an important meaning (this CO poisoning has so great influence that the operating temperature of a phosphoric acid fuel cell is low). And the gas which uses hydrogen as the main ingredients from CO transformer 5 as mentioned above will be supplied to the fuel electrode 3.

[0013]With the inverter 9, DC/AC conversion is carried out, and the direct current power from the fuel cell body 1 turns into alternating current power, and serves as the ac output 10 and the power supply 11 for plants. While stopping the inverter 9 in order to stop the reaction in a fuel cell when suspending power generation, purge gas is supplied to the air pole 2 or the fuel electrode 3. This purge gas is the inactive gas for severing oxygen or hydrogen, and N_2 is usually used. At this time, the power supply for plants changes from the electric power from the inverter 9 till then to an external power with the transfer device which is not illustrated.

[0014]While usually shifting to a power generation stop state from a power generation state, the state of adjustment power generation is established, power generation temperature is lowered, or a steam partial pressure is increased in a 1st embodiment of this invention, and it generates electricity for a while. Drawing 3 shows the relation between the temperature (**, K) of a phosphoric acid aqueous solution, and concentration (%) and the steam partial pressure (mmHg) of the open air. By concentration's falling and increasing a steam partial pressure also at the same temperature shows that concentration falls by from now on lowering the same steam partial pressure or temperature. Therefore, the concentration of a phosphoric acid aqueous solution can be lowered by lowering power generation temperature or increasing a steam partial pressure. Thereby, freezing of phosphoric acid is avoidable. Specifically during power generation, the place which is 200-150 ** is lowered to 100-120 **. And temperature, a steam partial pressure, and a generation output are controlled so that the concentration of phosphoric acid will be 79% and a phosphoric acid freezing point will be 0 **. In that case, as long as it seems that steams run short, the equipment (for example, an electric heater, a gas boiler, etc.) with which heat required for steam generating is compensated may be formed using external energy. As long as it is an electric heater, it may provide anywhere between the steam separator 6 or the steam separator 6, and the fuel cell body 1. As long as it is a gas boiler, it may provide anywhere along which the steam passes. Below, the concrete method for increasing a steam partial pressure is shown.

[0015](1) Make the steam/fuel ratio in the refining original fuel gas to the reformer 7 increase. Although the steam is supplied to the reformer 7 from the first, the ratio of the steam is increased. By this, the surplus water steam in reformed gas is increased, the water vapor content in fuel electrode distributed gas is increased as a result, and a steam partial pressure is increased. In this case, CO conversion (ratio which makes CO CO_2) increases, the influence of the battery characteristic fall by CO poisoning is reduced, and there is also a secondary effect that it is stabilized and power generation at low temperature can be performed.

[0016](2) Make a ratio of oxygen utilization or hydrogen utilization increase. When the steam partial pressure in distributed gas is lower than the steam partial pressure in the phosphoric acid concentration of a target, the steam partial pressure in the fuel cell body 1 can be increased raising the capacity factor of oxygen or hydrogen, i.e., by decreasing the amount of distributed gas. This is for the rate over the distributed gas of the water vapor content produced by power generation to increase. But it is more desirable to raise a ratio of oxygen utilization, since it is known that an electrode may deteriorate if hydrogen is made to run short.

[0017]Below, the load under adjustment power generation is explained. It is also considered during adjustment power generation that only the direct current voltage which is not enough to drive the inverter 9 is obtained. In that case, the dc output of the fuel cell body 1 is switched to the dummy load 13 with the switch 14 from the inverter 9, electric power required for the plant operation usually supplied from the inverter 9 is supplied from the outside, and a plant operation is made continuable. The electric power generated by adjustment power generation is consumed with the dummy load 13, and power generation is also continued. Depending on selection of the resistance of the dummy load 13, the voltage of the fuel cell body 1 rises too much, and it may lead to degradation of the catalyst of the fuel cell body 1. In order to avoid this, the voltage of the fuel cell body 1 makes the resistance of the dummy load 13 the value of the range which does not go up rather than a specified value. Although it presupposed that the change of load is based on the switch 14, it is desirable to make it become a smooth change actually.

[0018]According to a 2nd embodiment of this invention, a steam is supplied into the inactive gas which purges the fuel cell body 1 for the stop of the usual power generation or adjustment power generation. Thereby, a steam partial pressure can be increased and phosphoric acid concentration can be lowered. If dry inactive gas is supplied even if it lowers phosphoric acid concentration by adjustment power generation, phosphoric acid concentration may go up again, but this is also avoidable by supplying a steam. Also in this embodiment, the steam amount of supply should just be controlled so that the concentration of phosphoric acid will be 79% and a phosphoric acid freezing point will be 0 **. The steam to supply can also be generated using the remaining heat of a fuel cell immediately after power generation stops.

[0019]Below, the composition on the structure which supplies a steam is explained as a 3rd embodiment of this invention.

(1) Form the line L1 which supplies a steam into an air pole supply air from the steam generators (the steam separator 6, a boiler (not shown), etc.) inside a plant.

(2) Provide the line L3 and L4 which supply a steam into the reformed gas of fuel electrode 3 entrance from reformer 7 exit from the steam generator inside a plant. If the line L4 supplied between reformer 7 exit and CO transformer 5 is formed, it is effective in improving CO conversion and reducing CO poisoning.

(3) Provide the line (not shown) which supplies a steam into purge gas from the steam generator inside a plant.

(4) Provide the line (not shown) which supplies at least a part of purge gas via the inside of the steam generator inside a plant. If the temperature of the steam separator 6 is less than 100 **, generating of a steam will stop, but since the steam is still contained in the inside of the steam separator 6, thereby, a steam can be added to purge gas. By these composition, the stopping method of the above-mentioned phosphoric acid fuel cell is realizable.

[0020]

[Effect of the Invention]Therefore, according to this invention, phosphoric acid concentration adjustment before the prolonged storage of a phosphoric acid fuel cell can be performed economically and simple.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention]This invention relates to the method of stopping power generation in the state where phosphoric acid is not frozen even if it does not keep it warm at the time of the stopping method of a phosphoric acid fuel cell, especially prolonged storage, and the phosphoric acid fuel cell for it.

[Translation done.]

PRIOR ART

[Description of the Prior Art]Conventionally, the phosphoric acid fuel cell uses thick phosphoric acid as an electrolyte, and the usually employed density range is nearly 100%. The freezing temperature of phosphoric acid in the concentration of this neighborhood is near 40 ** (in 100%, it is 42.4 ** and referring to drawing 2). In the power generation state, since the temperature of a fuel cell body is as high as 150-200 ** (usually about 200 **), there is no possibility that phosphoric acid may freeze over, but if temperature falls even to a room temperature level when power generation is suspended, phosphoric acid is frozen and having serious influence on the characteristic of a fuel cell body is known.
[0003]When stopping a fuel cell temporarily, the measure of keeping a fuel cell body warm using a heater and other heating methods in order to prevent the characteristics degradation by this freezing is taken. When [required for incubation] energy source (power supply etc.) reservation cannot be carried out, or when a stop covers a long time, it is necessary to adjust phosphoric acid concentration to the low concentration which is a grade which phosphoric acid does not freeze from an economical viewpoint even if it does not carry out incubation. For example, if phosphoric acid concentration is reduced to about 78%, freezing temperature will fall to 0 ** (refer to drawing 2).
[0004]For this reason, phosphoric acid concentration is conventionally lowered after the power generation stop by holding a fuel cell body in a predetermined temperature and the atmosphere of a steam partial pressure. The conditions for making phosphoric acid into predetermined concentration can be searched for from the relation (refer to drawing 3) of the concentration of phosphoric acid, temperature, and the steam partial pressure on phosphoric acid. Setting out of a steam partial pressure is performed by circulating the gas which has a predetermined steam partial pressure to a fuel cell body.
[0005]For example, in JP,H7-169475,A, The method of carrying out humidification by the hygroscopic surface moisture in the air by introducing air into an air pole after a plant power generation stop is indicated, Hydrogen is introduced into a hydrogen pole after a plant power generation stop, a power generation reaction is caused in oxygen and the low temperature in the air of an air pole, and the method of diluting phosphoric acid concentration with the moisture generated as a result is indicated.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention]Therefore, according to this invention, phosphoric acid concentration adjustment before the prolonged storage of a phosphoric acid fuel cell can be performed economically and simple.

[Translation done.]

TECHNICAL PROBLEM

[Problem to be solved by the invention]However, in the case of the air condition (a steam partial pressure is low) dramatically dried like winter, enforcement is difficult in order to use the gas which tends to be influenced by the open air conditions of the water vapor of the air in conventional technology. By the time the steam amount of supply to a fuel cell body decreases and it reaches predetermined phosphoric acid concentration when a steam partial pressure is low even if it is a level of a feasible steam partial pressure, between a long time, for example, one to two days, may be needed dramatically, and there is a demerit in the field of personnel expenses and a power cost.
[0007]Also when introducing hydrogen after stopping a plant, there is a demerit that the expense of hydrogen itself, the expense of hydrogen supply equipment, etc. are needed. An object of this invention is to provide the stopping method of a phosphoric acid fuel cell and phosphoric acid fuel cell which can perform phosphoric acid concentration adjustment before the prolonged storage of a phosphoric acid fuel cell economically and simple.

[Translation done.]

* NOTICES *

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1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

MEANS

[Means for solving problem]While usually shifting to a power generation stop state from a power generation state, a stopping method of a phosphoric acid fuel cell of this invention lowers power generation temperature of a fuel cell body rather than usual, or is provided with an adjustment power generation procedure of making a steam partial pressure increasing and generating rather than usual. Since that it is what is generated so that equilibrium concentration of phosphoric acid may turn into prescribed concentration can make a predetermined thing phosphoric acid concentration after a power generation stop, said adjustment power generation procedure has it. [preferred]
[0009]Since that it is what uses external energy can compensate an insufficiency of a steam, said adjustment power generation procedure has it. [preferred] Said adjustment power generation procedure can increase a steam partial pressure because it is a thing to which that it is a thing to which the steam/fuel ratio in refining original fuel gas to this reformer are made to increase from usual, a ratio of oxygen utilization, or hydrogen utilization is made to increase from usual. Generated output can be connected to dummy load and the electric power required for operation of said phosphoric acid fuel cell can perform an adjustment power generation procedure in a low generation output by having an electric power supply procedure supplied from the outside.
[0010]Said electric power supply procedure can avoid that voltage of a fuel cell body rises too much, and a catalyst of a fuel cell body deteriorates because it is that by which power generation voltage of said phosphoric acid fuel cell controls resistance of said dummy load in a range which does not go up rather than a specified value. Since a stopping method of a phosphoric acid fuel cell of this invention shifts to a power generation stop state, it is provided with a purge procedure which supplies a steam into inactive gas which purges a fuel cell body.
[0011]At temperature after power generation stop completion, since that it is what supplies a steam so that equilibrium concentration of phosphoric acid may turn into prescribed concentration can make a predetermined thing phosphoric acid concentration after a power generation stop, said purge procedure has it. [preferred] A phosphoric acid fuel cell of this invention is a phosphoric acid fuel cell provided with a steam generator, and in an air pole supply air in reformed gas of a fuel electrode entrance from a reformer exit, Or a stopping method of the above-mentioned phosphoric acid fuel cell which is provided with a line which supplies a steam from said steam generator, and increases a steam partial pressure of a fuel cell body rather than usual by this into purge gas is realizable. In a phosphoric acid fuel cell provided with a steam generator, a phosphoric acid fuel cell of this invention is provided with a line which supplies at least a part of purge gas via inside of this steam generator.
[0012]
[Mode for carrying out the invention]Basic constitution of a phosphoric acid fuel cell is first explained using drawing 1. The fuel cell body 1 has structure which sandwiches the matrix 4 with the air pole 2 and the fuel electrode 3. Air which is the open air is supplied to the air pole 2, a part of oxygen is consumed by power generation, and the remaining air is exhausted. Gas which uses hydrogen as the main ingredients from CO transformer 5 is supplied to the fuel electrode 3, a part of hydrogen is consumed and the remainder is supplied to the burner 8 for reformers. The

matrix 4 is a sheet in which solution of phosphoric acid used as an electrolysis solution has sunk in. The fuel cell body 1 is cooled with water from the steam separator 6. Water for this cooling will be heated conversely, will contain a steam, is returned to the steam separator 6, and is separated from water. Therefore, this steam separator 6 is a steam generator. Raw materials and mineral fuel of gas which result in the fuel electrode 3 are hydrocarbon, such as town gas and LPG, and the reformer 7 is supplied with a steam supplied via the line L2 from the steam separator 6, become hot by the burner 8 for reformers, and the next chemical reaction is caused, CH_4+H_2O -> $CO+3H_2$ ... (1) $CO+H_2O$ -> CO_2+H_2 ... (2) hydrogen, CO, and CO_2 are generated. In this stage, a ratio of CO and CO_2 is about 10% respectively. And a reaction of (2) is further advanced by following CO transformer 5, and a ratio of CO is lowered even to about 1% by it. Since CO in fuel reduces the activity of a catalyst of the fuel cell body 1 (CO poisoning), making a ratio of CO small has an important meaning (this CO poisoning has so great influence that an operating temperature of a phosphoric acid fuel cell is low). And gas which uses hydrogen as the main ingredients from CO transformer 5 as mentioned above will be supplied to the fuel electrode 3.

[0013]With the inverter 9, DC/AC conversion is carried out, and direct current power from the fuel cell body 1 turns into alternating current power, and serves as the ac output 10 and the power supply 11 for plants. While stopping the inverter 9 in order to stop a reaction in a fuel cell when suspending power generation, purge gas is supplied to the air pole 2 or the fuel electrode 3. This purge gas is the inactive gas for severing oxygen or hydrogen, and N_2 is usually used. At this time, a power supply for plants changes from electric power from the inverter 9 till then to an external power with a transfer device which is not illustrated.

[0014]While usually shifting to a power generation stop state from a power generation state, a state of adjustment power generation is established, power generation temperature is lowered, or a steam partial pressure is increased in a 1st embodiment of this invention, and it generates electricity for a while. Drawing 3 shows relation between temperature (**, K) of a phosphoric acid aqueous solution, and concentration (%) and a steam partial pressure (mmHg) of the open air. By concentration's falling and increasing a steam partial pressure also at the same temperature shows that concentration falls by from now on lowering the same steam partial pressure or temperature. Therefore, concentration of a phosphoric acid aqueous solution can be lowered by lowering power generation temperature or increasing a steam partial pressure. Thereby, freezing of phosphoric acid is avoidable. Specifically during power generation, a place which is 200-150 ** is lowered to 100-120 **. And temperature, a steam partial pressure, and a generation output are controlled so that concentration of phosphoric acid will be 79% and a phosphoric acid freezing point will be 0 **. In that case, as long as it seems that steams run short, equipment (for example, an electric heater, a gas boiler, etc.) with which heat required for steam generating is compensated may be formed using external energy. As long as it is an electric heater, it may provide anywhere between the steam separator 6 or the steam separator 6, and the fuel cell body 1. As long as it is a gas boiler, it may provide anywhere along which a steam passes. Below, a concrete method for increasing a steam partial pressure is shown.

[0015](1) Make the steam/fuel ratio in the refining original fuel gas to the reformer 7 increase. Although the steam is supplied to the reformer 7 from the first, the ratio of the steam is increased. By this, the surplus water steam in reformed gas is increased, the water vapor content in fuel electrode distributed gas is increased as a result, and a steam partial pressure is increased. In this case, CO conversion (ratio which makes CO CO_2) increases, the influence of the battery characteristic fall by CO poisoning is reduced, and there is also a secondary effect that it is stabilized and power generation at low temperature can be performed.

[0016](2) Make a ratio of oxygen utilization or hydrogen utilization increase. When the steam partial pressure in distributed gas is lower than the steam partial pressure in the phosphoric acid concentration of a target, the steam partial pressure in the fuel cell body 1 can be increased raising the capacity factor of oxygen or hydrogen, i.e., by decreasing the amount of distributed gas. This is for the rate over the distributed gas of the water vapor content produced by power

generation to increase. But it is more desirable to raise a ratio of oxygen utilization, since it is known that an electrode may deteriorate if hydrogen is made to run short.

[0017]Below, the load under adjustment power generation is explained. It is also considered during adjustment power generation that only the direct current voltage which is not enough to drive the inverter 9 is obtained. In that case, the dc output of the fuel cell body 1 is switched to the dummy load 13 with the switch 14 from the inverter 9, electric power required for the plant operation usually supplied from the inverter 9 is supplied from the outside, and a plant operation is made continuable. The electric power generated by adjustment power generation is consumed with the dummy load 13, and power generation is also continued. Depending on selection of the resistance of the dummy load 13, the voltage of the fuel cell body 1 rises too much, and it may lead to degradation of the catalyst of the fuel cell body 1. In order to avoid this, the voltage of the fuel cell body 1 makes the resistance of the dummy load 13 the value of the range which does not go up rather than a specified value. Although it presupposed that the change of load is based on the switch 14, it is desirable to make it become a smooth change actually.

[0018]According to a 2nd embodiment of this invention, a steam is supplied into inactive gas which purges the fuel cell body 1 for a stop of the usual power generation or adjustment power generation. Thereby, a steam partial pressure can be increased and phosphoric acid concentration can be lowered. If dry inactive gas is supplied even if it lowers phosphoric acid concentration by adjustment power generation, phosphoric acid concentration may go up again, but this is also avoidable by supplying a steam. Also in this embodiment, the steam amount of supply should just be controlled so that concentration of phosphoric acid will be 79% and a phosphoric acid freezing point will be 0 **. A steam to supply can also be generated using remaining heat of a fuel cell immediately after power generation stops.

[0019]Below, composition on structure which supplies a steam is explained as a 3rd embodiment of this invention.

(1) Form the line L1 which supplies a steam into an air pole supply air from steam generators (the steam separator 6, a boiler (not shown), etc.) inside a plant.

(2) Provide the line L3 and L4 which supply a steam into reformed gas of fuel electrode 3 entrance from reformer 7 exit from a steam generator inside a plant. If the line L4 supplied between reformer 7 exit and CO transformer 5 is formed, it is effective in improving CO conversion and reducing CO poisoning.

(3) Provide the line (not shown) which supplies a steam into purge gas from the steam generator inside a plant.

(4) Provide the line (not shown) which supplies at least a part of purge gas via the inside of the steam generator inside a plant. If the temperature of the steam separator 6 is less than 100 **, generating of a steam will stop, but since the steam is still contained in the inside of the steam separator 6, thereby, a steam can be added to purge gas. By these composition, the stopping method of the above-mentioned phosphoric acid fuel cell is realizable.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]The figure explaining the composition of this invention phosphoric acid fuel cell.
[Drawing 2]The figure showing the relation between the concentration of a phosphoric acid aqueous solution, and freezing temperature.
[Drawing 3]The figure showing the relation between the concentration of a phosphoric acid aqueous solution, temperature, and the steam partial pressure on phosphoric acid.
[Explanations of letters or numerals]
1 Fuel cell body
2 Air pole
3 Fuel electrode
4 Matrix
5 CO transformer
6 Steam separator
7 Reformer
8 The burner for reformers
9 Inverter
10 Ac output
11 The power supply for plants
13 Dummy load
14 Switch
L1-L4 Steam supply line

[Translation done.]

(19)日本国特許庁（ＪＰ）　(12) **公開特許公報**（Ａ）　(11)特許出願公開番号

特開平11－154529

(43)公開日　平成11年(1999)６月８日

(51)Int.Cl.^{6}	識別記号	ＦＩ	
Ｈ０１Ｍ　8/04		Ｈ０１Ｍ　8/04	Ｙ
			Ｆ

審査請求　未請求　請求項の数13　ＯＬ　（全５頁）

(21)出願番号　特願平9－321097

(22)出願日　平成９年(1997)11月21日

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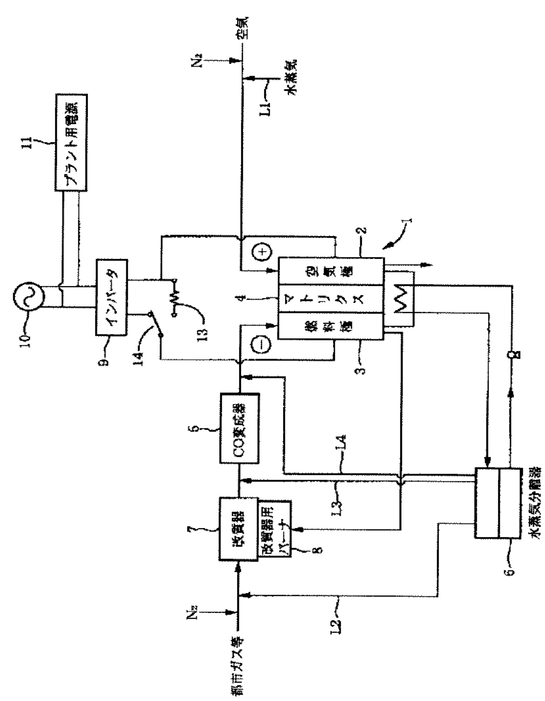
(54)【発明の名称】　リン酸型燃料電池の停止方法及びリン酸型燃料電池

(57)【要約】

【課題】　リン酸型燃料電池の長期保管前のリン酸濃度調整を経済的かつ簡便に行うことができる、リン酸型燃料電池の停止方法及びリン酸型燃料電池を提供すること。

【解決手段】　空気極２、燃料極３、マトリクス４から成る燃料電池本体１に対して、通常発電状態から発電停止状態へ移行する間に、水蒸気分離器６で発生する水蒸気をラインＬ３を介して改質器７からの改質ガス中に供給することで、燃料極３に供給される水蒸気を増加させて、水蒸気分圧を上昇させてマトリクス４のリン酸濃度を下げる。これにより、リン酸の氷結温度を下げて燃料電池を室温に下げてもリン酸が凍結しないようにする。



【特許請求の範囲】

【請求項１】　通常発電状態から発電停止状態へ移行する間に、燃料電池本体の、発電温度を通常よりも下げて、又は、水蒸気分圧を通常よりも上げて、発電させる調整発電手順を備えることを特徴とするリン酸型燃料電池の停止方法。

【請求項２】　前記調整発電手順は、リン酸の平衡濃度が所定濃度になるように発電するものであることを特徴とする請求項１記載のリン酸型燃料電池の停止方法。

【請求項３】　前記調整発電手順は、外部のエネルギーを用いるものであることを特徴とする請求項１又は２記載のリン酸型燃料電池の停止方法。

【請求項４】　前記リン酸型燃料電池は、炭化水素と水とから水素を発生させる改質器を備え、前記調整発電手順は、該改質器への改質原燃料ガス中の水蒸気／燃料比を通常よりも増加させるものであることを特徴とする請求項１乃至３いずれかに記載のリン酸型燃料電池の停止方法。

【請求項５】　前記調整発電手順は、酸素利用率又は水素利用率を通常よりも増加させるものであることを特徴とする請求項１乃至４いずれかに記載のリン酸型燃料電池の停止方法。

【請求項６】　前記リン酸型燃料電池は、ダミー負荷を備え、さらに、通常発電状態から発電停止状態へ移行する間に、発電電力を該ダミー負荷に接続し、前記リン酸型燃料電池の運転に必要な電力は外部から供給する電力供給手順を備えることを特徴とする請求項１乃至５いずれかに記載のリン酸型燃料電池の停止方法。

【請求項７】　前記電力供給手順は、前記リン酸型燃料電池の発電電圧が所定値よりも上昇しない範囲に前記ダミー負荷の抵抗値を制御するものであることを特徴とする請求項６記載のリン酸型燃料電池の停止方法。

【請求項８】　発電停止状態に移行するため燃料電池本体をパージする不活性ガス中に水蒸気を供給するパージ手順を備えることを特徴とするリン酸型燃料電池の停止方法。

【請求項９】　前記パージ手順は、発電停止完了後の温度において、リン酸の平衡濃度が所定濃度になるように水蒸気を供給するものであることを特徴とする請求項８記載のリン酸型燃料電池の停止方法。

【請求項１０】　水蒸気発生器を備えるリン酸型燃料電池において、空気極供給空気中に該水蒸気発生器から水蒸気を供給するラインを備えることを特徴とするリン酸型燃料電池。

【請求項１１】　水蒸気発生器を備えるリン酸型燃料電池において、炭化水素と水とから水素を発生させる改質器の出口から燃料極入口の改質ガス中に該水蒸気発生器から水蒸気を供給するラインを備えることを特徴とするリン酸型燃料電池。

【請求項１２】　水蒸気発生器を備えるリン酸型燃料電池において、パージガス中に該水蒸気発生器から水蒸気を供給するラインを備えることを特徴とするリン酸型燃料電池。

【請求項１３】　水蒸気発生器を備えるリン酸型燃料電池において、パージガスの少なくとも一部を該水蒸気発生器内を経由して供給するラインを備えることを特徴とするリン酸型燃料電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、リン酸型燃料電池の停止方法、特に長期保管時に保温を施さなくてもリン酸が凍結しない状態で発電を停止させる方法、及び、そのためのリン酸型燃料電池に関するものである。

【０００２】

【従来の技術】従来、リン酸型燃料電池は電解質として濃厚リン酸を用いており、通常運用する濃度範囲は１００％近辺である。この付近の濃度におけるリン酸の氷結温度は４０℃付近である（１００％において４２．４℃、図２参照）。発電状態においては、燃料電池本体の温度は１５０～２００℃（通常は約２００℃）と高いのでリン酸が氷結するおそれはないが、発電を停止した場合に室温レベルまで温度が低下すると、リン酸が凍結し、燃料電池本体の特性に重大な影響を与えることが知られている。

【０００３】一時的に燃料電池を停止する場合は、この凍結による特性低下を防止する目的で燃料電池本体をヒータその他の加熱手段を用いて保温するという対策が講じられている。また、保温のために必要なエネルギー源（電源等）確保できない場合や、停止が長時間にわたる場合には経済的な観点から、保温を実施しなくてもリン酸が凍結しない程度の低濃度までリン酸濃度を調整する必要がある。例えば、リン酸濃度を約７８％まで低下させると、氷結温度は０℃まで下がる（図２参照）。

【０００４】このため、従来は発電停止後に、燃料電池本体を所定の温度、水蒸気分圧の雰囲気に保持することにより、リン酸濃度を下げている。リン酸を所定の濃度にするための条件は、リン酸の濃度、温度、リン酸上の水蒸気分圧の関係（図３参照）から求めることができる。なお、水蒸気分圧の設定は、所定の水蒸気分圧を有するガスを燃料電池本体に流通することにより行われる。

【０００５】例えば、特開平７－１６９４７５号公報においては、プラント発電停止後に空気極に空気を導入することにより、空気中の湿分による加湿を実施する方法を開示し、また、プラント発電停止後に水素極に水素を導入し、空気極の空気中の酸素と低温において発電反応を起こし、その結果生成する水分によりリン酸濃度を希釈する方法を開示している。

【０００６】

【発明が解決しようとする課題】しかし、従来技術で

は、大気中の水蒸気という外気条件に左右されやすいガスを使用するために、冬季のように非常に乾燥した（水蒸気分圧の低い）空気の状態の場合には実施が困難である。また、実施可能な水蒸気分圧のレベルであったとしても、水蒸気分圧が低い場合には、燃料電池本体への水蒸気供給量が減少し、所定のリン酸濃度に到達するまでに、非常に長時間、例えば、１～２日間を必要とする場合があり、人件費、動力費の面でのデメリットがある。

【０００７】さらに、プラントを停止後に水素を導入する場合にも、水素自体の費用、水素供給設備の費用等が必要になるというデメリットがある。本発明は、リン酸型燃料電池の長期保管前のリン酸濃度調整を経済的かつ簡便に行うことができる、リン酸型燃料電池の停止方法及びリン酸型燃料電池を提供することを目的とするものである。

【０００８】

【課題を解決するための手段】本発明のリン酸型燃料電池の停止方法は、通常発電状態から発電停止状態へ移行する間に、燃料電池本体の、発電温度を通常よりも下げて、又は、水蒸気分圧を通常よりも上げて、発電させる調整発電手順を備えるものである。また、前記調整発電手順は、リン酸の平衡濃度が所定濃度になるように発電するものであることが、発電停止後のリン酸濃度を所定のものにすることができるので、好ましい。

【０００９】さらに、前記調整発電手順は、外部のエネルギーを用いるものであることが、水蒸気の不足分を補うことができるので、好ましい。また、前記調整発電手順は、該改質器への改質原燃料ガス中の水蒸気／燃料比を通常よりも増加させるものであること、又は、酸素利用率又は水素利用率を通常よりも増加させるものであることで、水蒸気分圧を上げることができる。また、発電電力をダミー負荷に接続し、前記リン酸型燃料電池の運転に必要な電力は外部から供給する電力供給手順を備えることで、低発電出力での調整発電手順を実行することができる。

【００１０】また、前記電力供給手順は、前記リン酸型燃料電池の発電電圧が所定値よりも上昇しない範囲に前記ダミー負荷の抵抗値を制御するものであることで、燃料電池本体の電圧が上昇し過ぎて、燃料電池本体の触媒が劣化することを避けることができる。また、本発明のリン酸型燃料電池の停止方法は、発電停止状態に移行するため燃料電池本体をパージする不活性ガス中に水蒸気を供給するパージ手順を備えるものである。

【００１１】さらに、前記パージ手順は、発電停止完了後の温度において、リン酸の平衡濃度が所定濃度になるように水蒸気を供給するものであることが、発電停止後のリン酸濃度を所定のものにすることができるので、好ましい。また、本発明のリン酸型燃料電池は、水蒸気発生器を備えるリン酸型燃料電池であって、空気極供給空気中に、改質器出口から燃料極入口の改質ガス中に、又は、パージガス中に、前記水蒸気発生器から水蒸気を供給するラインを備えるものであり、これにより燃料電池本体の水蒸気分圧を通常よりも上げる、上記のリン酸型燃料電池の停止方法を実現することができる。さらに、本発明のリン酸型燃料電池は、水蒸気発生器を備えるリン酸型燃料電池において、パージガスの少なくとも一部を該水蒸気発生器内を経由して供給するラインを備えるものである。

【００１２】

【発明の実施の形態】図１を用いて、まずリン酸型燃料電池の基本構成を説明する。燃料電池本体１は空気極２及び燃料極３でマトリクス４をサンドイッチする構造となっている。空気極２には外気である空気が供給され、発電により酸素の一部が消費されて残りの空気は排気される。燃料極３にはＣＯ変成器５から水素を主成分とするガスが供給され、水素の一部が消費され、残りは改質器用バーナ８へ供給される。マトリクス４は電解液となるリン酸の水溶液がしみ込んでいるシートである。燃料電池本体１は水蒸気分離器６からの水によって冷却される。この冷却用の水は逆に熱せられて水蒸気を含むことになり、水蒸気分離器６に戻されて、水と分離される。したがって、この水蒸気分離器６は水蒸気発生器になっている。燃料極３に到るガスの原燃料は都市ガス、ＬＰＧ等の炭化水素であって、水蒸気分離器６からラインＬ２を介して供給される水蒸気と共に改質器７へ供給され、改質器用バーナ８で熱せられて、次の化学反応を起こして、$CH_4+H_2O \rightarrow CO+3H_2$　・・・　(1)　$CO+H_2O \rightarrow CO_2+H_2$　・・・　(2)水素とＣＯとCO_2を発生する。この段階で、ＣＯとCO_2の比率は約１０％ずつである。そして、次のＣＯ変成器５によって、更に(2)の反応が進められてＣＯの比率を約１％にまで下げる。燃料中のＣＯは、燃料電池本体１の触媒の活性を低下させるので（ＣＯ被毒）、ＣＯの比率を小さくすることには重要な意味がある（このＣＯ被毒はリン酸型燃料電池の運転温度が低いほど影響が大きい）。そして、前記のようにＣＯ変成器５から水素を主成分とするガスが燃料極３に供給されることになる。

【００１３】燃料電池本体１からの直流電力はインバータ９によってＤＣ／ＡＣ変換されて交流電力となり、交流出力１０及びプラント用の電源１１となる。発電を停止するときには、燃料電池での反応を停止させるために、インバータ９を停止させるとともに、空気極２又は燃料極３にパージガスを供給する。このパージガスは酸素又は水素を絶つための不活性ガスであり、通常はN_2が使われる。この時、プラント用の電源は図示しない切替装置により、それまでのインバータ９からの電力から、外部電源に切り替わる。

【００１４】本発明の第１の実施の形態では、通常発電状態から発電停止状態へ移行する間に調整発電の状態を設けて、発電温度を下げるか又は水蒸気分圧を上げて、

しばらく発電する。図３は、リン酸水溶液の温度（℃、Ｋ）と、濃度（％）と外気の水蒸気分圧（ｍｍＨｇ）との関係を示している。これから、同じ水蒸気分圧でも、温度を下げることによって濃度が下がり、また、同じ温度でも、水蒸気分圧を上げることによって濃度が下がることがわかる。したがって、発電温度を下げるか又は水蒸気分圧を上げることによってリン酸水溶液の濃度を下げることができる。これによりリン酸の凍結を避けることができる。具体的には、発電中には２００～１５０℃であるところを１００～１２０℃に下げる。そして、リン酸の濃度が例えば７９％、すなわち、リン酸凍結温度が０℃となるように、温度、水蒸気分圧、そして、発電出力を制御する。その際、水蒸気が不足するようであれば外部のエネルギーを用いて、水蒸気発生に必要な熱を補う装置（例えば電気ヒータやガスボイラー等）を設けても良い。それが電気ヒータであれば、水蒸気分離器６又は水蒸気分離器６と燃料電池本体１との間のどこに設けても良い。それがガスボイラーであれば、水蒸気が通っているところのどこに設けても良い。つぎに、水蒸気分圧を上げるための具体的な方法を示す。

【００１５】(1) 改質器７への改質原燃料ガス中の水蒸気／燃料比を増加させる。改質器７へはもともと水蒸気が供給されているが、その水蒸気の比率を多くするのである。これにより、改質ガス中の余剰水蒸気を増やし、結果として燃料極供給ガス中の水蒸気量を増やして、水蒸気分圧を上げる。また、この場合に、ＣＯ転化率（ＣＯをCO_2にする比率）が上がり、ＣＯ被毒による電池特性低下の影響が低減され低温での発電を安定して行えるという副次的効果もある。

【００１６】(2) 酸素利用率又は水素利用率を増加させる。供給ガス中の水蒸気分圧が、目標のリン酸濃度における水蒸気分圧より低い場合には、酸素又は水素の利用率を上げること、すなわち、供給ガス量を減少することにより、燃料電池本体１での水蒸気分圧を上げることができる。これは発電によって生じる水蒸気量の供給ガスに対する割合が増加するためである。もっとも、水素を欠乏させると電極が劣化する場合があることが知られているので、酸素利用率を上げる方が望ましい。

【００１７】つぎに、調整発電中の負荷について説明する。調整発電中はインバータ９を駆動するのに十分でない直流電圧しか得られないことも考えられる。その際には、燃料電池本体１の直流出力をインバータ９からダミー負荷１３にスイッチ１４によって切換え、通常はインバータ９から供給されるプラント運転に必要な電力を外部から供給して、プラント運転を継続可能にする。調整発電によって発生される電力はダミー負荷１３によって消費されることで、発電も継続される。また、ダミー負荷１３の抵抗値の選定によっては、燃料電池本体１の電圧が上昇し過ぎて、燃料電池本体１の触媒の劣化につながることがある。これを避けるため、ダミー負荷１３の抵抗値は燃料電池本体１の電圧が所定値よりも上昇しない範囲の値とする。なお、負荷の切換えはスイッチ１４によるとしたが、実際には滑らかな切換えとなるようにすることが望ましい。

【００１８】本発明の第２の実施の形態では、通常の発電又は調整発電の停止のために、燃料電池本体１をパージする不活性ガス中に水蒸気を供給する。これにより、水蒸気分圧を上げてリン酸濃度を下げることができる。また、調整発電によりリン酸濃度を下げても、乾燥した不活性ガスを供給してしまうと、再びリン酸濃度が上がる可能性もあるが、水蒸気を供給することでこれを避けることもできる。本実施の形態の場合も、リン酸の濃度が例えば７９％、すなわち、リン酸凍結温度が０℃となるように、水蒸気供給量を制御すれば良い。供給する水蒸気は、発電が停止した直後の燃料電池の余熱を利用して、発生させることもできる。

【００１９】つぎに、本発明の第３の実施の形態として、水蒸気を供給する構造上の構成について説明する。

(1) プラント内部の水蒸気発生器（水蒸気分離器６やボイラー（図示せず）等）から空気極供給空気中に水蒸気を供給するラインＬ１を設ける。

(2) プラント内部の水蒸気発生器から、改質器７出口から燃料極３入口の改質ガス中に水蒸気を供給するラインＬ３、Ｌ４を設ける。改質器７出口とＣＯ変成器５との間に供給するラインＬ４を設ければ、ＣＯ転化率を向上してＣＯ被毒を低減する効果もある。

(3) プラント内部の水蒸気発生器からパージガス中に水蒸気を供給するライン（図示せず）を設ける。

(4) パージガスの少なくとも一部を、プラント内部の水蒸気発生器内を経由して、供給するライン（図示せず）を設ける。水蒸気分離器６の温度が１００℃を下回ると水蒸気の発生は停止するが、水蒸気分離器６の内部には依然として水蒸気が含まれているので、これにより、パージガスに水蒸気を加えることができる。これらの構成により、上記リン酸型燃料電池の停止方法を実現することができる。

【００２０】

【発明の効果】したがって、本発明によれば、リン酸型燃料電池の長期保管前のリン酸濃度調整を経済的かつ簡便に行うことができる。

【図面の簡単な説明】

【図１】本発明リン酸型燃料電池の構成を説明する図。

【図２】リン酸水溶液の濃度と氷結温度との関係を示す図。

【図３】リン酸水溶液の濃度と温度とリン酸上の水蒸気分圧の関係を示す図。

【符号の説明】

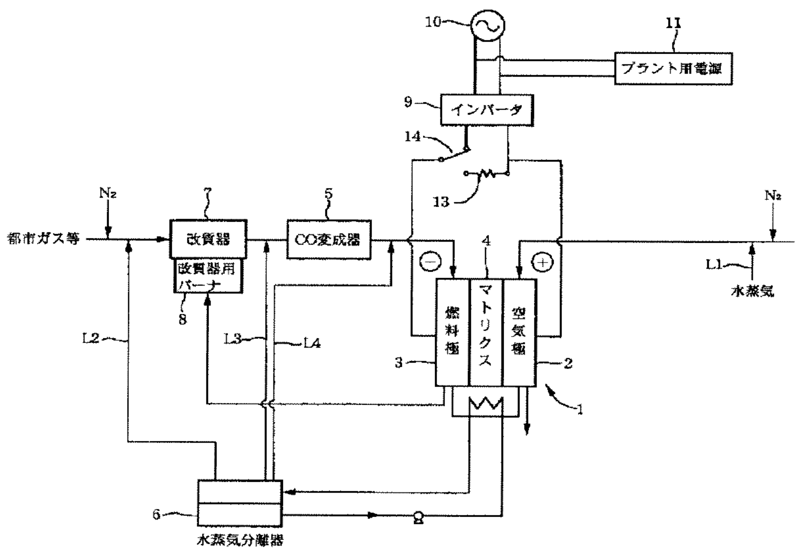
１　燃料電池本体

２　空気極

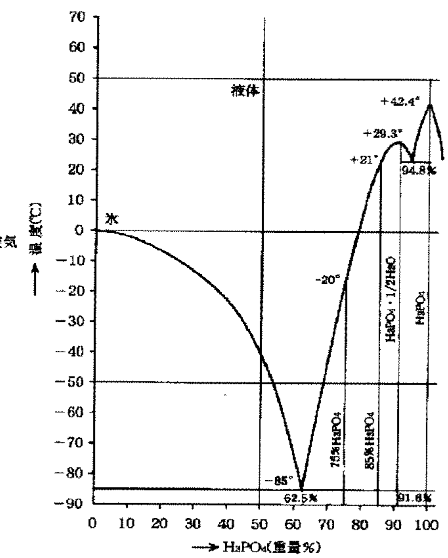
３　燃料極

4　マトリクス
5　ＣＯ変成器
6　水蒸気分離器
7　改質器
8　改質器用バーナ
9　インバータ
１０　交流出力
１１　プラント用電源
１３　ダミー負荷
１４　スイッチ
Ｌ１～Ｌ４　水蒸気供給ライン

【図１】



【図２】



【図３】